

AD-A281 592



REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

This is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and reviewing the collection of information, sending comments regarding this burden estimate or any other aspect of this reporting burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Avenue, Washington, DC 20503, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

2. REPORT DATE

6/16/94

3. REPORT TYPE AND DATES COVERED

Final Report 5/1/91 - 4/30/94

Synthesis of Tungsten Nitrene Complexes as Precursors for Tungsten Nitride

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DAAL03-91-G-0130

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

ARO 28353.7-CH

11. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Chemical vapor deposition using organometallic precursors (MOCVD) provides a method for the preparation of thin films. Low valent tungsten nitrene complexes were synthesized as potential precursors to tungsten nitride (WN_x), a material used in diffusion barriers for Si or GaAs semiconductor devices. The original target precursors for MOCVD of WN_x were the carbonyl-containing complexes $(CO)_{5-n}(PR_3)_nW=NR$, where R is an alkyl or aryl group. Later synthetic work involved the tungsten(IV) imido (or nitrene) complexes $(CO)_2I_2LW=NPh$, which were prepared by oxidation of the zwitterionic species $(CO)_5WNPPhNPhC(OMe)Ph$ with one equivalent of I_2 followed by addition of a the coordinating species L [L= THF, pyridine, PMe_3 , $P(OMe)_3$].

DTIC QUALITY INSPECTED 8

14. SUBJECT TERMS

low valent nitrene complex, tungsten nitride, MOCVD precursors

15. NUMBER OF PAGES

3

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

UL

94-21416



Final Report

1. ARO PROPOSAL NUMBER: 28253-CH
2. PERIOD COVERED BY REPORT: 1 May 1991 - 30 April 1994
3. TITLE OF PROPOSAL: Synthesis of Tungsten Nitrene Complexes as Precursors to Tungsten Nitride
4. GRANT NUMBER: DAAL03-91-G-0130
5. NAME OF INSTITUTION: Stanford University
6. AUTHOR OF REPORT: Lisa McElwee-White
7. STATEMENT OF PROBLEM:

Distribution /	
Availability Codes	
Dist	Avail and / or Special
A-1	

Chemical vapor deposition using organometallic precursors (MOCVD) provides a method for the preparation of thin films. We are developing syntheses of low valent tungsten nitrene complexes as precursors to tungsten nitride (WN_x), a material used in diffusion barriers for Si or GaAs semiconductor devices. Our target precursors for MOCVD of WN_x are the carbonyl-containing complexes $(CO)_{5-n}(PR_3)_nW=NR$, where R is an alkyl or aryl group. Upon heating at a surface, these compounds should lose the five ancillary ligands and undergo fragmentation of the NR group to deposit a film of WN_x .

8. SUMMARY OF MOST IMPORTANT RESULTS:

Previously generated complexes of the type $(CO)_5W=NR$ such as $(CO)_5W=NPh$ ($Ph = C_6H_5$) had been far too unstable to isolate and thus unsuitable as MOCVD precursors. We predicted that changing from a hydrocarbon R group to a nitrogen-containing one would result in a dramatic stabilization of the $(CO)_5W=NR$ complex. These predictions were borne out upon synthesis of $(CO)_5W=NNMe_2$, which was much more stable than $(CO)_5W=NPh$ but still not sufficiently robust for MOCVD. Additional stability could be obtained via substitution of the CO ligands by bulky phosphines that provided steric protection for the reactive nitrene nitrogen. Reaction of $(CO)_5W=NNMe_2$ with phosphines of increasing steric bulk resulted in a series of complexes of increasing stability culminating with the crystalline solid $(CO)_3(dppe)W=NNMe_2$ [$dppe = 1,2$ -bis(diphenylphosphino)ethane], which is indefinitely stable at room temperature.

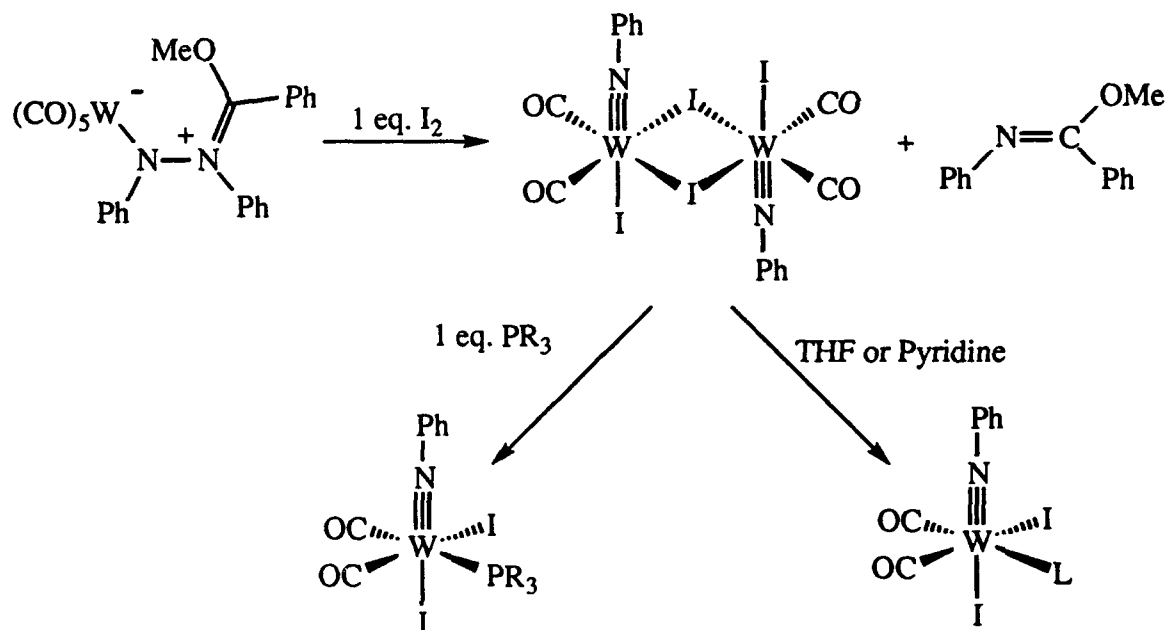
After establishing that both electron-donation and steric bulk do indeed increase the stability of these complexes, we explored the relative importance of each and worked to find molecules that are similar in stability to $(CO)_3(dppe)W=NNMe_2$ but with lower molecular weights so that they would be more volatile for MOCVD. Studies on the sterically protected (but not electronically stabilized) complexes $(CO)_5W=NR$ where R = triphenylmethyl or triptycyl served to place a limit on the effectiveness of steric protection at N. Although these molecules are easily prepared from $(CO)_5W(THF)$ and the alkyl azide, they decompose at $-78^\circ C$ by a combination of aryl shift and hydrogen abstraction pathways. Thus, steric protection at N is not sufficient and electronic stabilization of the complexes by NR_2 substituents apparently will be necessary for effective MOCVD precursors.

We also examined derivatives of the stable complex $(CO)_3(dppe)W=NNMe_2$ where dppe has been replaced by the slightly smaller ligand dmpe [$dmpe = 1,2$ -bis(diphenylphosphino)methane]. The dmpe derivative also formed a stable crystalline

solid for which we have obtained an X-ray structure. However, the smaller ligand results in a highly unusual binding mode in which the ligand bridges from the metal to the nitrene nitrogen to form a metallacycle.

We have recently begun to explore the chemistry of tungsten (IV) imido complexes bearing CO ligands. The new target complexes were molecules of the type $(\text{CO})_2\text{I}_2\text{LW}\equiv\text{NPh}$. These species maintain the CO ligands that should be good leaving groups during MOCVD of tungsten nitride but the higher oxidation state renders the metal nitrene (or imido) moiety much more stable than in the zero-valent nitrene complexes studied in the earlier stages of the project. We had previously reported that the zwitterionic complex $(\text{CO})_5\text{WNPhNPhC(OMe)Ph}$ decomposes upon thermolysis or photolysis to yield $(\text{CO})_5\text{W}\equiv\text{NPh}$. We have now demonstrated that this species is also a precursor to the tungsten (IV) imido complexes since the zwitterion can serve as a protected imido functionality during oxidation of the metal center. Treatment of the zwitterionic complex $(\text{CO})_5\text{WNPhNPhC(OMe)Ph}$ with one equivalent of I_2 leads to the formation of highly unusual iodo-bridged tungsten (IV) imido dimer $[(\text{CO})_2\text{I}_2\text{W}\equiv\text{NPh}]_2$ and $\text{PhN}=\text{C(OMe)Ph}$ (Scheme 1). Cleavage of the dimer with coordinating species leads to formation of the monomeric compounds $(\text{CO})_2\text{I}_2\text{LW}\equiv\text{NPh}$. These complexes are now being explored as MOCVD precursors in collaboration with Professor Timothy J. Anderson, Department of Chemical Engineering, University of Florida.

Scheme 1



9. LIST OF PUBLICATIONS:

1. "Metathesis and Diaziridination Reactions of $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{-p-XC}_6\text{H}_4$ with cis-Azobenzene. Electronic and Solvent Effects," Maxey, C.T.; Sleiman, H.F.; Massey, S.T.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 5153-5160.
2. "Stabilization of Zero-Valent Hydrazido Complexes by Phosphine Ligands. Crystal Structure of fac- $(\text{CO})_3(\text{DPPE})\text{W}=\text{NNMe}_2$, a Nitrene Analogue to Fischer Carbenes," Arndtsen, B.A.; Schoch, T.K.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 7041-7047.
3. "Structure of (Benzo[c]cinnoline-N')pentacarbonyl; tungsten," Pham, E.K.; McElwee-White, L. *Acta Crystallographica* **1992**, *C48*, 1120-1121.
4. "Electrophilic Reactions of Zero-Valent Tungsten Nitrene and Hydrazido Complexes with Phosphines. Synthesis and Structure of $(\text{CO})_4\text{W}(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{NNMe}_2)$." Arndtsen, B.A.; Sleiman, H.F.; McElwee-White, L.; Rheingold, A.L. *Organometallics*, **1993**, *12*, 2440-2444.
5. "Reactions of $(\text{CO})_5\text{W}(\text{THF})$ with Triphenylmethyl Azide and Triptycyl Azide," Massey, S.T.; Mansour, B.; McElwee-White, L. *J. Organomet. Chem.*, in press.
6. "Tungsten (IV) Imido Complexes From Oxidation of a Protected Zero-Valent Nitrene Precursor," McGowan, P.C.; Massey, S.T.; Abboud, K.A.; McElwee-White, L. *J. Am. Chem. Soc.*, in press.

10. PARTICIPATING SCIENTIFIC PERSONNEL:

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Postdoctorals: Dr. Patrick C. McGowan
Dr. Nicholas D.R. Barnett

Graduate Students and Postdoctorals received stipends, undergraduates received only research supplies.